



Consommation
et Corporations Canada
Bureau des brevets
Ottawa, Canada
K1A 0C9

Consumer and
Corporate Affairs Canada
Patent Office

(11) (C) 1,293,356
(21) 506,345
(22) 1986/04/10
(45) 1991/12/24
(52) 23-261

5
(51) INTL.CL. C22B-34/12; C01G-23/053; C01B-17/90

(19) (CA) CANADIAN PATENT (12)

(54) Process for the Production of Titanium Dioxide

(72) Gerken, Rudolf , Germany (Federal Republic of)
Lailach, Günter , Germany (Federal Republic of)
von Deuten, Klaus , Germany (Federal Republic of)

(73) Bayer Aktiengesellschaft , Germany (Federal Republic of)

(30) (DE) Germany (Federal Republic of) P 35 13 120.9
1985/04/12

(57) 10 Claims

Canada

CCA 3254 (10-89) 41

BEST AVAILABLE COPY

506345

A process for the production of titanium dioxide

Abstract of the Disclosure

The present invention relates to a process for the production of titanium dioxide by discontinuous digestion of titanium slag with sulphuric acid, production of a titanyl sulphate solution suitable for hydrolysis from the solid digestion cake obtained during digestion, hydrolysis of the titanyl sulphate, separation and calcination of the titanium-containing hydrolyzate, evaporation of the waste acid separated from the hydrolyzate and re-use of the sulphuric acid separated from the evaporated waste acid in the digestion of titanium slag.

A process for the production of titanium dioxide

5

The present invention relates to a process for the production of titanium dioxide by discontinuous digestion of titanium slag with sulphuric acid, production of a titanyl sulphate solution suitable for hydrolysis from the solid digestion cake obtained during digestion, hydrolysis of the titanyl sulphate, separation and calcination of the titanium-containing hydrolyzate, evaporation of the waste acid separated from the hydrolyzate and re-use of the sulphuric acid separated from the evaporated waste acid in the digestion of titanium slag.

The requirement for recycling of sulphuric acid from the TiO_2 production process by the sulphate process is having to be met more and more. In addition to the expected economic disadvantages in comparison with dumping of waste acid in the ocean, the process often encounters technical problems.

A process for working up waste acids is known from DE-A 3 327 769 and is adopted on an industrial scale. Depending on the local condition, however, problems can arise here if the waste acid is to be almost completely recycled.

According to the working up process currently adopted, the waste acid is concentrated, preferably by multi-stage vacuum evaporation, until a 60 to 70% sulphuric acid with a low content of dissolved metal sulphates can be separated by filtration from crystallized metal sulphates.

35

Le A 23 707

5 The concentration of this recovered sulphuric acid
is generally too low, however, to produce a sulphuric acid
initial concentration suitable for the discontinuous
digestion of raw material when mixed with fresh sulphuric
acid or oleum, which is required for replacing the sul-
phuric acid losses (by metal sulphate binding, residual
10 moisture in the separated metal sulphates, waste water).
It is therefore necessary further to evaporate the sul-
phuric acid separated from the metal sulphates, and this
can be effected, for example, by using the waste heat from
 TiO_2 calcination (EP-A 97 259).

15 The greater the content of recycled sulphuric acid
in the total mixture, the higher the concentration of the
recycled acid must be. As the concentration increases,
however, the requirements in energy and equipment also
increase. In particular, when using the titanium slags
20 which are advantageous from an ecological point of view
as raw material, a particularly high concentration of the
recycled acid is required if maximum possible industrial
recycling is desired.

25 A more desirable situation arises if the relatively
low sulphuric acid losses during digestion of the titanium
slags can be replaced by 95 to 98% sulphuric acid ("fresh
acid") instead of oleum. The production of oleum can thus
be omitted.

30 In this case, according to the prior art it is only
possible to concentrate recycling acid in a high concen-
tration apparatus (for example a Pauling distillation
vessel) to about 96% (Ullmanns Encyklopädie d. techn.
Chemie, 4th edition, volume 18, page 579, Verlag Chemie,

35

Le A 23 707

5 Weinheim 1979). However, this stage of the process is extremely expensive with respect both to the investment costs and to the energy and maintenance costs.

10 It is accordingly the object of the present invention to propose a method which overcomes the above-mentioned disadvantages of the prior art in an economical manner.

15 This object can surprisingly be achieved by the following combination of measures:

- evaporation of the 60 to 75% sulphuric acid separated from the metal sulphates and containing dissolved metal sulphates under vacuum in horizontal or circulation evaporators at from 120 to 190°C to 76 to 87% H₂SO₄ (based on salt-free sulphuric acid),
- mixing of the ground titanium slag with 95 to 98% sulphuric acid at from 30 to 80°C and addition of the recycled acid at a temperature of from 80 to 190°C, preferably from 100 to 160°C.

20 The present invention accordingly relates to a process for the production of titanium dioxide by discontinuous digestion of titanium slag with sulphuric acid, production of a titanyl sulphate solution suitable for hydrolysis from the solid digestion cake obtained during digestion, hydrolysis of the titanyl sulphate, separation and calcination of the titanium-containing hydrolyzate, evaporation of the waste acid separated from the hydrolyzate and re-use of the sulphuric acid separated from the evaporated waste acid in titanium slag digestion, a 60 to 75% pre-concentrated sulphuric acid being separated from the solid metal sulphates and hydrogen sulphates after

25

30
Le A 23 707

5 evaporation of the waste acid, this sulphuric acid being further evaporated under vacuum to a concentration of between 76 to 87% H₂SO₄ (calculated as salt-free sulphuric acid) and being used together with 95 to 98% sulphuric acid in the digestion of the ground titanium slag.

10 The invention also teaches the conditions under which the titanium slag is to be digested in order to keep the necessary concentration of the recycled sulphuric acid and therefore the costs of sulphuric acid concentration as low as possible.

15 The titanium slag is advantageously mixed with warm 95 to 98% sulphuric acid ("fresh acid") at from 30 to 80°C, preferably from 50 to 80°C.

20 Digestion is initiated by addition of the uncooled or slightly cooled recycled acid, supplied from sulphuric acid evaporation to the warm fresh acid/slag mixture. The process corresponding to the prior art involving initiating digestion by addition of water or introduction of steam would require a substantially higher concentration of the recycled acid than the process according to the invention.

25 A particularly preferred embodiment of the process according to the invention therefore involves initiating the digestion reaction by addition of hot 76 to 87% sulphuric acid ("recycled acid") at from 80 to 190°C, preferably from 100 to 160°C.

30 A further reduction in the minimum sulphuric acid concentration required for discontinuous slag digestion by 2 to 3%, without losses of TiO₂ yield occurring, is successful because steam is blown through the digestion cake instead of air during the maturing time once the 35 maximum reaction temperature has been reached.

- 5 In a particularly desirable embodiment of the process according to the invention, the concentration of the sulphuric acid is advantageously between 87 and 91%, preferably 88 and 90% H₂SO₄ (calculated as solids-free and salt-free acid) at the start of the digestion reaction and
10 from 35 to 70% of the required sulphuric acid is recovered as recycled acid from the process.
- The necessary temperatures of the fresh acid and the recycled acid can be lowered according to the invention by grinding the titanium slag more finely.
- 15 The production of the 76 to 87% acid from 60 to 75% pre-concentrated sulphuric acid is preferably carried out by evaporation at from 120 to 190°C and from 40 to 150 mbar.
- 20 Horizontal evaporators with tantalum heat exchangers or circulation evaporators are particularly suitable for these evaporation processes not only for reasons of energy consumption.
- 25 Valuation of the process according to the invention has to consider the fact that secondary energy can be used instead of primary energy for producing the recycled acid and that the investment and maintenance costs are substantially lower compared with the prior art.
- The drawing serves to illustrate the process according to the invention.
- 30 The fresh acid (1) required for the digestion of raw material is mixed in the digestion reactor (3) or in a preceding mixer with the ground titanium slag (2) (optionally with addition of ground ilmenite). The fresh acid should have a temperature of from 30 to 80°C, preferably from 50 to 80°C. The necessary quantity of
35

Le A 23 707

recycled acid (17) is introduced at a temperature of from
5 80 to 190°C, preferably from 100 to 160°C, into the
digestion reactor (3) while blowing air through the
mixture present and the exothermal reaction is thus
initiated. If steam (4) which is at least 150°C hot is
blown in instead of air once the maximum reaction temper-
10 ature has been attained, the temperature drop of the
digestion mixture can be reduced and the TiO₂ yield
improved. After a maturing time of from 5 to 8 hours,
after which, from experience, no further improvement in
15 the TiO₂ yield can be expected, the digestion cake is
dissolved with water or preferably with sulphuric acid-
containing waste water (5) from the TiO(OH)₂ hydrolyzate
filtration process.

The titanyl sulphate solution is prepared in known
20 manner for hydrolysis. During the hydrolysis process (6),
sulphuric acid-containing waste water (5) is preferably
used as diluent water. The hydrolyzate (8) is calcined in
known manner to titanium dioxide (10).

The metal sulphate-containing sulphuric acid (waste
25 acid) (11) produced during filtration (7) normally has a
concentration of from 20 to 27% H₂SO₄. It can be pre-
evaporated using process heat before being evaporated in
known manner in an evaporator which is preferably a
30 multistage vacuum evaporator (12) until most of the metal
sulphates are crystallized and a 60 to 75% sulphuric acid
remains (= evaporation 1).

After cooling the suspension supplied from the
evaporation I to from 40 to 70°, the metal sulphates (14)
are separated from the sulphuric acid, preferably by
filtration (13).

35

5 The metal sulphates are partly in the form of
hydrogen sulphates and contain 60 to 75% sulphuric acid
as moisture. It is therefore advantageous to decompose
this "filter salt" thermally with formation of SO₂ and to
produce therefrom the 95 to 98% sulphuric acid required
as fresh acid. However, reaction with Ca compounds (DE-A
10 3 327 770) or a different harmless elimination process is
also possible.

15 Sulphuric acid losses occur mainly through the filter
salt, but also through the moisture of the solid residues
resulting from raw material digestion, the sulphuric acid
bound in the TiO(OH)₂ and the unavoidable waste water. As
pre-concentrated acid, therefore, only about 40 to 60% of
the sulphuric acid used during digestion can be recovered.
With 60 to 75% H₂SO₄, however, the concentration of this
acid is too low to allow autothermal slag digestion in
20 mixture with the necessary amount of from 95 to 98% fresh
acid.

25 The pre-concentrated acid (15) which still contains
about 3 to 6% by weight of dissolved metal sulphates
therefore must be evaporated in an evaporation II (16) to
76 to 87% H₂SO₄ (as salt-free acid), before it can be
recycled (17) for the digestion of the raw material. The
evaporation II (16) is carried out according to the invention
by vacuum evaporation at 120 to 190°C. Circulation
30 evaporators or horizontal evaporators with tantalum heat
exchangers can be used as evaporator systems. Horizontal
evaporators are preferred owing to the particularly high
specific evaporation capacity (with respect to the
tantalum heat exchanger surface). Preheating of the pre-

35.

Le A 23 707

concentrated sulphuric acid almost to boiling point is
5 advantageous (at a given evaporation pressure). Steam-
heated graphite heat exchangers are preferred for the
preheating operation. Cooling of the recycled acid
supplied from the evaporator is omitted or is optionally
10 carried out using the pre-concentrated acid introduced as
a cooling liquid, only until the temperature of the
recycled acid is still sufficient to initiate the di-
gestion reaction in the manner described above, i.e. until
the temperature lies in the range of from 80 to 190°C.

15 A substantial advantage of the process according to
the invention lies in the fact that problems which arise
during further cooling of this acid are avoided by using
the recycled acid at a temperature of from 80 to 190°C
because the metal sulphates dissolved in that acid (about
20 4 to 7% by weight) crystallize in an extremely finely
divided form at lower temperatures. As these salts tend
to settle on cool surfaces, they lead to frequent inter-
ruptions in the operation. These problems can be avoided
by introducing the recycled acid at a temperature at which
the dissolved metal sulphates not yet crystallize.

25 The process according to the invention, which is
substantially more economical than conventional high
concentration processes according to the prior art
evaporating sulphuric acid to about 96% H₂SO₄ and
initiating the digestion reaction by introduction of
30 steam into the sulphuric acid-slag mixture will be
described with reference to the following non-limiting
Examples.

35

Le A 23 707

Example 1 Comparison Example)

5

17.5 t of ground titanium slag were mixed with 18 t of metal sulphate-containing recycled acid and with 13.6 t of fresh 96% sulphuric acid (20°C). The digestion reaction was initiated by addition of 1.4 t of water and introduction of 0.6 t of steam. The maximum reaction temperature of 203°C was attained after 10 minutes. After initiation of the reaction, air was blown through the mixture (for 30 minutes at 350 m³/h, then for 7 hours at 20 m³/h). After a maturing time of 7 hours, the digestion cake had a temperature of 169°C. The TiO₂ yield was 95.3%.

20 The digestion cake was dissolved with a proportion of the sulphuric acid-containing waste water from the hydrolyzate filtration (5.4% by weight H₂SO₄). After working up the titanyl sulphate solution, the mixture was hydrolysed using a further proportion of the sulphuric acid-containing waste water as diluent water.

25 85 t of waste acid containing 23.2% H₂SO₄ and 29.8% SO₄²⁻(total) were separated from the hydrolyzate filtration process. The waste acid was evaporated in a 2-stage vacuum evaporator until the sulphuric acid (calculated as salt-free acid) had a concentration of 66% H₂SO₄. 31 t of 5 bar steam were used up for evaporating 47.5 t of H₂O.

30 11.3 t of sulphuric acid-containing filter cake were separated from the metal sulphate-sulphuric acid suspension after cooling to 55°C. The pre-concentrated acid (25.7 t) contained 62.8% of H₂SO₄, 32.4% of H₂O and 4.8% of dissolved metal sulphates.

35

Le A 23 707

introduced had a temperature of 89°C and the discharged
5 recycled acid had a temperature of 145°C. Only 4.94 t of
H₂O had to be evaporated instead of 5.7 t of H₂O. The
total energy consumption for the production of the
recycled acid from pre-concentrated acid and the blowing
of steam through the digestion cake was 19,460 kJ in
10 comparison with 22,700 kJ in Example 2.

Example 4

Laboratory experiments were carried out to examine
15 how the temperature of the recycled acid can be lowered
without problems arising due to an excessively slow rate
of the digestion reaction. 500 g of slag ground to varying
finenesses were mixed with 520 g of 96% sulphuric acid and
preheated to the temperature T₁. The mixture was then
20 mixed in an insulated vessel with 590 g of pure 85% sul-
phuric acid having a temperature of T₂. The mixture was
stirred while introducing 250 l of air/h and the temper-
ature gradient was recorded. The experimental results are
25 compiled in Table 1. T₃ is the temperature of the mixture
after addition of the 85% sulphuric acid and T₄ the
maximum temperature attained. t is the time period until
the maximum temperature is attained after addition of the
85% acid.

30

35

Le A 23 707

Table 1

5

		Exp. Fineness of grinding	T ₁ No. % by weight <40 µm	T ₂ [°C]	T ₃ [°C]	T ₄ [°C]	t [min]
10	1	81		50	110	76	-
	2	81		50	140	91	106
	3	81		70	140	101	154
	4	81		80	140	109	193
	5	81		70	160	117	192
	6	100		50	120	86	168
15	7	100		50	140	95	185
							28

The experimental results show that the temperature of the recycled acid can be lower if the titanium slag is ground more finely (Experiment 7) than with a coarser grinding (Experiment 2) achieving approximately the same reaction rate. Also the temperature of the 96% fresh acid can obviously be lowered instead of the temperature of the recycled acid.

The slower rise in the temperature of the laboratory digestions in comparison with the rise in temperature on an industrial scale is due to the relatively high thermal losses.

30

35

Le A 23 707

THE EMBODIMENTS OF THE INVENTION IN WHICH AN EXCLUSIVE PROPERTY OR PRIVILEGE IS CLAIMED ARE DEFINED AS FOLLOWS:

1. A process for the production of titanium dioxide by discontinuous digestion of titanium slag with sulphuric acid, the production of a titanyl sulphate solution suitable for hydrolysis from the solid digestion cake obtained during digestion, hydrolysis of the titanyl sulphate, separation and calcination of the titanium-containing hydrolyzate, evaporation of the waste acid separated from the hydrolyzate and re-use of the sulphuric acid separated from the evaporated waste acid in the digestion of titanium slag, characterized in that, after evaporation of the waste acid from the solid metal sulphates and hydrogen sulphates, a 60 to 75% pre-concentrated sulphuric acid is separated and is further evaporated under vacuum to a concentration of between 76 and 87% H_2SO_4 (calculated as salt-free sulphuric acid) and is used together with 95 to 98% sulphuric acid in the digestion of the ground titanium slag.
2. A process according to claim 1, wherein the titanium slag is mixed with warm 95 to 98% sulphuric acid ("fresh acid") at from 30 to 80°C.
3. A process according to claim 2, wherein the fresh acid is mixed at from 50 to 80°C.
4. A process according to claim 1, 2 or 3, wherein the digestion reaction is initiated by addition of hot 76 to 87% sulphuric acid ("recycled acid") at from 80 to 190°C.

5. A process according to claim 1, 2 or 3, wherein the digestion reaction is initiated by addition of hot 76 to 87% sulphuric acid ("recycled acid") at from 100 to 160°C.
6. A process according to claim 1, 2 or 3, wherein the concentration of the sulphuric acid is between 87 and 91%, H₂SO₄ (calculated as solids-free and salt-free acid) at the beginning of the digestion reaction and from 35 to 70% of the sulphuric acid required is recovered from the process as recycled acid.
7. A process according to claim 1, 2 or 3, wherein the concentration of the sulphuric acid is between 88 and 90% H₂SO₄ (calculated as solids-free and salt-free acid) at the beginning of the digestion reaction and from 35 to 70% of the sulphuric acid required is recovered from the process as recycled acid.
8. A process according to claim 1, 2 or 3, wherein the production of the 76 to 87% acid from 60 to 75% pre-concentrated sulphuric acid is effected by evaporation at from 120 to 190°C and from 40 to 150 mbar.
9. A process according to claim 1, 2 or 3, wherein the production of the 76 to 87% acid from 60 to 75% pre-concentrated sulphuric acid is effected by evaporation at from 120 to 190°C and from 40 to 150 mbar and a horizontal evaporator with a tantalum heat exchanger is used as evaporator.
10. A process according to claim 1, 2 or 3, wherein the production of the 76 to 87% acid from 60 to 75% pre-concentrated sulphuric

1293356

- 16 -

23189-6235

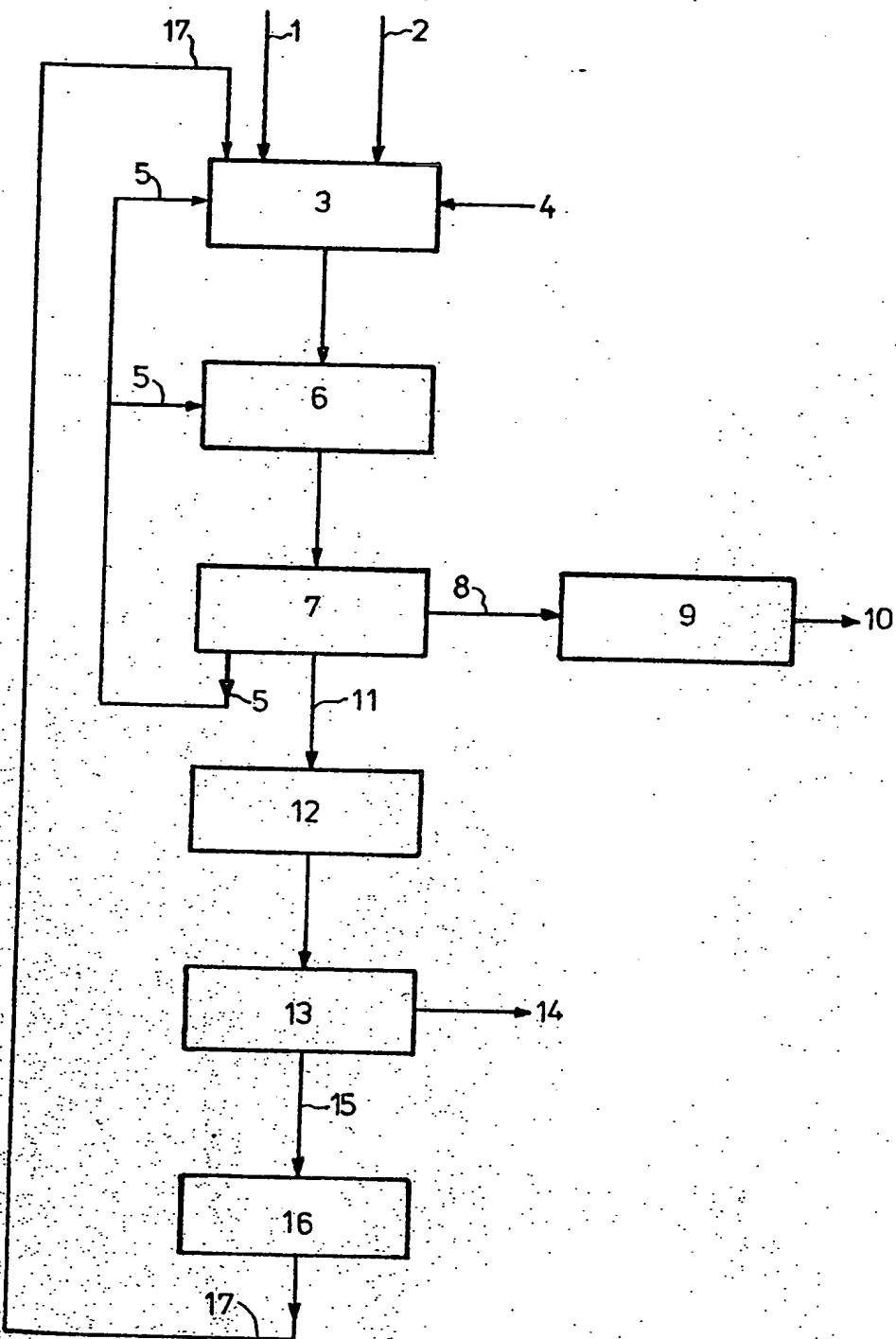
acid is effected by evaporation at from 120 to 190°C and from 40 to 150 mbar and a circulation evaporator is used as evaporator.

FETHERSTONHAUGH & CO.
OTTAWA, CANADA

PATENT AGENTS

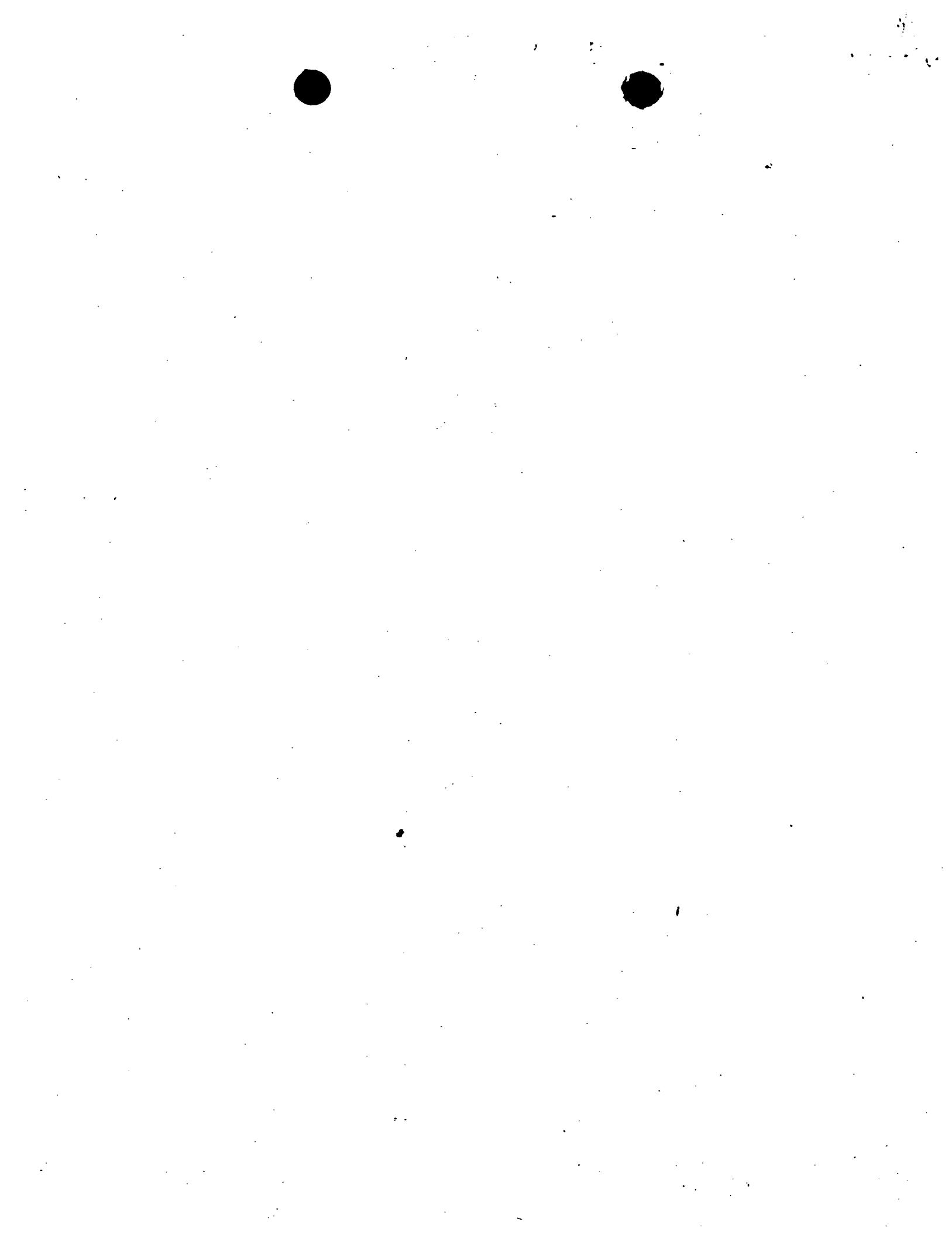


- 16 -



Le A 23 707

Paten Agents
Birmingham & L.



**This Page is Inserted by IFW Indexing and Scanning
Operations and is not part of the Official Record**

BEST AVAILABLE IMAGES

Defective images within this document are accurate representations of the original documents submitted by the applicant.

Defects in the images include but are not limited to the items checked:

- BLACK BORDERS**
- IMAGE CUT OFF AT TOP, BOTTOM OR SIDES**
- FADED TEXT OR DRAWING**
- BLURRED OR ILLEGIBLE TEXT OR DRAWING**
- SKEWED/SLANTED IMAGES**
- COLOR OR BLACK AND WHITE PHOTOGRAPHS**
- GRAY SCALE DOCUMENTS**
- LINES OR MARKS ON ORIGINAL DOCUMENT**
- REFERENCE(S) OR EXHIBIT(S) SUBMITTED ARE POOR QUALITY**
- OTHER:** _____

IMAGES ARE BEST AVAILABLE COPY.

As rescanning these documents will not correct the image problems checked, please do not report these problems to the IFW Image Problem Mailbox.

THIS PAGE BLANK (USPTO)